

THE RELEASE OF NITROGEN IN THE COMBUSTION AND PYROLYSIS OF COALS AND MACERALS

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Introduction

The release of nitrogen and sulphur oxides during coal combustion is a major environmental problem. NO_x and SO_x are contributors to acid rain whereas N_2O is a 'greenhouse' gas. In coal combustion the following stages occur: 1) rapid devolatilization followed by 2) ignition of volatiles and 3) the slower char gasification [1]. The nitrogen and sulphur species are partitioned into the volatiles and the char. The minimization of the environmental impact of coal combustion by improved burner technology and flue gas desulphurization is currently underway. In the case of NO_x emissions, the retrofitting of 'low NO_x ' burners in power stations has been undertaken. In these combustion systems, the char nitrogen is the major contributor to NO_x emissions [2]. The volatiles are released in a zone where the oxygen concentration is low and the formation of molecular nitrogen is favoured. Therefore the release of nitrogen and sulphur oxides during coal combustion has major implications for the environment.

The release of nitrogen oxides is controlled to an extent by the combustion conditions but there are also variations due to coal properties [3-5]. In low NO_x burners and fluidized bed combustion, fuel nitrogen is the major contributor to NO_x formation. Therefore an understanding of the nitrogen in coal and its release during combustion is an important consideration. Coals are a complex heterogeneous material with a cross-linked macromolecular structure. This gives rise to problems when characterising the coal for combustion purposes. This structural heterogeneity can be described at a variety of levels. At the macroscopic level coals may have a banded structure. At the microscopic level the structure may be described as microscopic components, macerals or associations of macerals which are termed microlithotypes. Macerals can be separated and have distinct physical and chemical properties, for example, volatile matter, nitrogen content, reactivity etc. When considering coal the heterogeneity must be considered since the small particles used in pulverised fuel (pf) combustion, depending on the coal, may be regarded as pure macerals or associations of macerals [6-9]. When considering the nitrogen in coal at the molecular level the nitrogen functionality must be considered. The nitrogen may be described as pyrrolic, pyridinic or quaternary nitrogen.

The objective of this paper was to study the release of coal nitrogen as NO_x during temperature programmed combustion of coals and macerals, with the emphasis being on the identification of reactive intermediate species and a comparison of the differences between macerals.

Experimental

Materials used

The characterisation data for the coals and maceral concentrates used in this study are given in Table 1. Maceral concentrates were obtained by the density gradient centrifugation (DGC) technique [10-12].

Temperature Programmed Combustion

The temperature programmed combustion studies were carried out using a Thermal Sciences thermogravimetric analysis - mass spectrometer system (TG-MS). This system consisted of a thermogravimetric analysis (TGA) instrument coupled with a VG Quadrupoles 300 amu mass spectrometer. Gas sampling was carried out at two positions: 1) approximately 1 cm directly above the sample and 2) at the exit of the thermogravimetric analyser. The former sampling point allows reactive intermediate species to be detected while the latter essentially samples the gases at equilibrium. The evolved gas profiles were measured at both sampling positions. Approximately 5 mg of the coal was used in each run. The sample was heated at 15 K min^{-1} in 20% oxygen/helium and the evolved gas profiles recorded. The following mass/charge (m/z) ratios were monitored throughout the course of the reaction: 2, 14-65.

Temperature Programmed Pyrolysis

The temperature programmed pyrolysis was carried out in argon at a flow rate of 50 cc min^{-1} at a heating rate of 15 K min^{-1} in a similar manner to the combustion experiments. In this case gas sampling was carried out at the exit of the thermogravimetric analyser.

Results

A comparison of the temperature programmed combustion required evolved gas profiles for Illinois No. 6, in 20% oxygen/helium with sampling directly above the sample and at the exit of the thermogravimetric analyser. These are shown in Figures 1(a) and 1(b) respectively. It is apparent that whilst there are similarities between the two sets of evolved gas profiles there are also marked differences. The profiles have a complex series of emissions. The integrated gas concentration ratios for some of the species evolved during the temperature programmed combustion of the Illinois No. 6 coal are given in Table 2. The CO and CO₂ profiles show a shoulder on the low temperature side. This corresponds to the evolution of small hydrocarbons and tars. In addition, the CO/CO₂ ratios for gas sampling directly above the sample and at the exit of the thermogravimetric analyser were 0.535 and 0.096 respectively. This clearly indicates that CO is being formed and released into the gas phase where it is converted to CO₂ by homogeneous gas phase reactions. Another noticeable difference in intensities is the increase in m/z 30 concentration and decrease in m/z 27 concentration when comparing sampling directly above the sample and at the exit of the TGA. This can be explained by the conversion of HCN released in the gas combustion process and converted to NO by gas phase oxidation reactions. The fraction of coal nitrogen converted to NO is 0.362 when measured by sampling directly above the sample and this increases to 0.961 when the gas sampling is carried out at the exit of the TGA. Not all of the m/z 27 and m/z 30 are HCN and NO respectively. Undoubtedly there are small contributions from hydrocarbons, and/or fragmentation in the mass spectrometer which make a contribution for some m/z ratios. When gas sampling is carried out directly above the sample, a high CO concentration is observed. Since NO is in relatively low concentration, there may be a significant contribution to the NO peak from $^{12}\text{C}^{18}\text{O}$. This

contribution can be corrected for by subtracting $0.002 \cdot \text{CO}$ peak. The peak which occurs at the lowest temperature $\sim 300^\circ\text{C}$ is consistent with the release of hydrocarbons. This precedes the release of tars when the coal starts to pyrolyse. Figure 1(a) shows that intermediate species such as COS and HCN are released during the temperature programmed combustion. Evolved gas profiles have been monitored for all m/z values in the range 14-65. It is apparent that when gas sampling is carried out directly above the sample many of the masses have weak profiles. It is difficult to assign the peaks unequivocally to various species due to the complex nature of the mixture of gases evolved and fragmentation effects in the mass spectrometer. However, it is apparent that in some coals, a peak was observed for m/z 52 at the beginning of the char gasification region whereas no corresponding peaks were observed at m/z 51 and 53. This peak was observed at the same temperatures as peaks at m/z 26 and 27 corresponding to HCN and its fragments. Therefore it is reasonable to assign the peak at m/z 52 to $(\text{CN})_2$. The evolved gas profiles for m/z 41, 42 and 43 were all bimodal. The lowest temperature peak for m/z 43 occurs at a position coincident with m/z values which can be assigned to the evolution of small hydrocarbon species. The higher temperature peak for m/z 43 which occurs at a similar temperature to m/z 52 and 27 is possibly due, in part, to HOCN. The evolved gas profiles at 41, 42, 43, 52, 60 etc are either not observed or are very weak when gas sampling is carried out at the exit of thermogravimetric analyser thereby confirming that reactive intermediate species can be detected by gas sampling close to the sample during temperature programmed combustion. A suite of coals with a range of rank have been studied in detail, in addition, to the coal described above. These include Blind Canyon and Pocohontas from the Argonne Premium Coal Sample Bank and Illinois No. 6 from SBN. These reveal significant differences in the release of species such as COS, $(\text{CN})_2$ etc. during temperature programmed combustion.

The corresponding temperature programmed pyrolysis profiles are shown in Figure 1(c). In this case the gas sampling was carried out at the exit of the TGA. The results show that a range of small gaseous molecules CO_2 , CO, NO, N_2 , HCN, SO_2 and CH_4 are evolved over a range of temperatures. At the lowest temperatures low molar mass hydrocarbons were detected. Tars were condensed out and not detected. It is apparent that the temperature programmed pyrolysis technique is capable of distinguishing the release of gaseous species. Some of the peaks, for example, m/z 27 (HCN) occurs at the same temperature for both the pyrolysis and combustion.

The temperature programmed combustion evolved gas profiles for the entrained flow reactor chars prepared from Illinois No. 6 are shown in Figure 2. The results show similarities to the temperature programmed combustion of the raw coal. The CO concentration measured by sampling directly above the sample is high but this is reduced when evolved gas sampling is carried out at the exit. The CO/CO_2 ratio decreases from 0.355 measured directly above the sample to 0.076 measured at the exit of the TGA. It is apparent that the primary product CO is again converted to CO_2 by gas phase homogeneous reactions as in the coal studies. In addition the m/z 27 peak (mainly HCN) virtually disappears and the m/z 30 (NO) increases slightly when gas sampling is carried out at the exit. The fraction of char nitrogen converted to NO measured directly above the sample was 0.225 and this increased to 0.399 when measured at the exit of the TGA. This is similar to the results for the corresponding coals but the effect is much smaller. This is consistent with the HCN released being converted to NO in the gas phase. Reactive species released during temperature programmed coal combustion, for example, COS, are not observed when gas sampling is carried out at the exit of the TGA.

The temperature programmed combustion evolved gas profiles for vitrinite (density 1.2 - 1.27 g cm⁻³) and fusinite (density 1.5 - 1.60 g cm⁻³) with gas sampling directly above the sample and at the exit of the TGA are given in Figure 3. As expected the vitrinite profiles are very similar to those obtained for raw coals with a pronounced shoulder on the low temperature side of the evolved gas profile. The corresponding CO and CO₂ profiles for the fusinite are more complex consisting of several peaks and reach a maximum at a higher temperature than the vitrinite fraction as expected from the lower reactivity of the inertinite fraction. This is observed when gas sampling is carried out at both directly above the sample and at the exit of the TGA. The observation that the CO and CO₂ evolved gas profiles of the fusinite are more complex than the profiles of the vitrinite fraction may be due to a number of factors. The samples were prepared by the DGC and it may be that different types of inertinite fraction are being resolved in the temperature programmed combustion. Also, higher concentrations of mineral matter were observed in the fusinite fraction and this may give rise to catalytic gasification effects. The NO evolved gas profile for the fusinite showed a peak at ~300°C followed by profile in the char gasification region which could be resolved into three peaks with similar temperatures to the CO and CO₂ profiles. The m/z 27 (mainly HCN) evolved gas profiles for gas sampling directly above the sample for the vitrinite and fusinite are both bimodal but these peaks virtually disappear when sampling is carried out at the exit of the TGA. It is surprising that the m/z 27 peaks occur at a higher temperature in the vitrinite concentrate than the fusinite. This may indicate structural differences. The m/z 14 peak is also bimodal when gas sampling is carried out directly above the sample. The high temperature peak in the profile is also observed when gas sampling is carried out at the exit of the TGA. This suggests that this peak is due to nitrogen.

The integrated gas concentration ratios for some of the species evolved in the temperature programmed combustion of the macerals are given in Table 2. A comparison of gas concentration ratios obtained when sampling directly above the sample and at the exit of the TGA shows similar trends to those observed for the raw coals. It is evident from the CO/CO₂ ratio that substantial amounts of CO formed in the combustion are converted in the gas phase to CO₂. Similarly a comparison of the two sampling positions indicates that the NO/N ratio is higher while the (m/z 27)/N i.e. mainly HCN/N, was virtually absent when gas sampling is carried out at the exit of the TGA. This is most probably due to the conversion of HCN and other nitrogen containing species to NO in the gas phase and is similar to the results obtained for the coals.

Discussion

Temperature programmed combustion is a useful technique for studying the release of nitrogen and sulphur species during the combustion of coals and chars. The evolved gas profiles have the following general characteristics [7, 8, 13-16].

1. For coals, there is a shoulder on the low temperature side of the CO and CO₂ evolved gas profiles for the coals. This shoulder corresponds to the release of low molecular mass species and tars and it is absent in the corresponding evolved gas profiles of the chars.
2. The release of NO and HCN during temperature programmed combustion is complex with several peaks. For low rank coals the NO peak is observed for the release of volatiles and the gasification of the char. The latter is sometimes asymmetric consisting of a number of peaks.

3. The NO profiles for the chars are delayed relative to the CO and CO₂ profile. The NO profiles always reach a maximum at a higher temperature than the corresponding CO₂ profiles. As a result the NO/CO₂ and NO/CO profiles usually increase with increasing burn-off. The NO/CO and NO/CO₂ ratios tend to decrease in the region where volatiles are released from the coals.

In this study, two gas sampling positions have been used: 1) ~1 cm above the sample and 2) at the exit of the thermogravimetric analyser. The results of this study show that reactive intermediate species can be detected by sampling close to the sample undergoing combustion. Some of the reactive species which have been identified are COS, (CN)₂, HCN and CO as well as hydrocarbon species. These species are either not detected or are observed in very much lower concentrations for sampling at the exit of the TGA. These studies have shown that under temperature programmed conditions there are a number of well defined stages which can be assigned to the release of low molecular mass gases, tars and combustion products and char gasification. Therefore the thermogravimetric analyser - mass spectrometer allows the extent of gas phase reactions to be assessed. In comparison, pyrolysis studies can also be carried out under temperature programmed conditions.

Previous temperature programmed combustion studies [6-9, 13-16] of a suite of coals and chars covering a wide range of rank have shown that the fraction of coal/char nitrogen converted to NO decreases with increasing reactivity. These studies were carried out with the gas sampling directly above the sample. In the case of the coals, substantial amounts of HCN were detected and if this were assumed to be converted to NO this would modify the trend for conversion of the coal nitrogen to NO for gas sampling at that position. In these studies the suite of coals studied covered a range of reactivities. Therefore the nitrogen species are released over the different temperature ranges. The release of the NO may vary with temperature and this may be a factor which influences the observed trend. Isothermal reactivity studies have also shown that a similar correlation exists [16] between char reactivity and the fraction of char nitrogen converted to NO. Hence it is apparent from the trends that gas sampling of the temperature programmed combustion of the coals allows reactive nitrogen species to be detected and that the NO release is similar to that for the char. The results of a more detailed investigation show that a range of reactive species can be detected.

Conclusions

The use of temperature programmed combustion for studying the release of reactive intermediate species from coal has been investigated. It is apparent that a comparison of gas sampling carried out directly above the sample and at the exit of the TGA shows that reactive species can be detected. Species detected include CO, COS, HCN, (CN)₂. The conversion of the nitrogen intermediate species to NO has been followed by the technique. It is apparent that temperature programmed combustion is a useful technique for following the release of nitrogen and sulphur during coal and char combustion.

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Table 1 Characterisation data for the coal, char, and maceral concentrates.

Coal/ Maceral	Illinois No6 (APCS) Coal	Illinois No6 (APCS) Char	Coal A Vitrinite	Coal A Fusinite
Proximate Analysis				
Volatile Matter (daf)/ %	47.39	4.43	41.97	35.76
Ash (dry)/ %	15.48	29.84	1.21	31.26
Elemental Analysis				
C (daf)/ %	77.67	99.63	82.57	79.01
H (daf)/ %	5.00	0.67	5.28	4.25
N (daf)/ %	1.37	1.82	1.72	0.83
O (daf)/ %	13.51		12.16	15.68
Random Relectance/ %	0.43	0.43	0.65	0.65
Maceral Analysis				
Vitrinite/ %	85.00			
Liptinite/ %	5.00			
Inertinite/ %	10.00			
Minerals/ %	18.10			

Table 2 Temperature programmed combustion evolved gas concentration ratios

Sample	CO/ CO ₂	NO/ N	HCN/ N
Illinois No6 (APCS) Coal			
-Above the Sample	0.535	0.362	0.209
-At the Exit	0.096	0.961	0.036
Illinois No6 (APCS) Char			
-Above the Sample	0.355	0.225	0.096
-At the Exit	0.076	0.399	0.016
Coal A Vitrinite Concentrate			
-Above the Sample	0.606	0.356	0.167
-At the Exit	0.067	0.546	0.025
Coal A Fusinite Concentrate			
-Above the Sample	0.314	0.797	0.325
-At the Exit	0.082	0.893	0.053

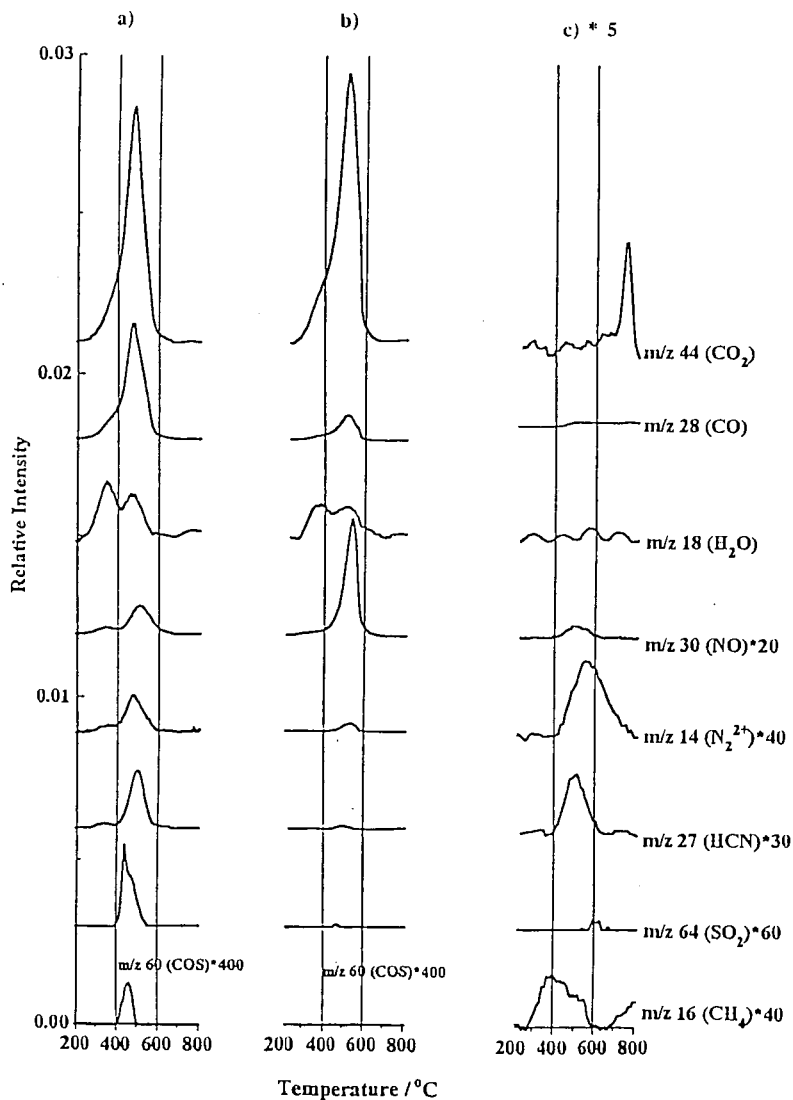


Figure 1 Temperature programmed evolved gas profiles for Illinois No6 (Argonne) coal in a) 20% oxygen/ helium with gas sampling directly above the sample, b) in 20% oxygen/ helium with gas sampling at the exit of the thermogravimetric analyser and c) in argon with gas sampling at the exit of the thermogravimetric analyser.

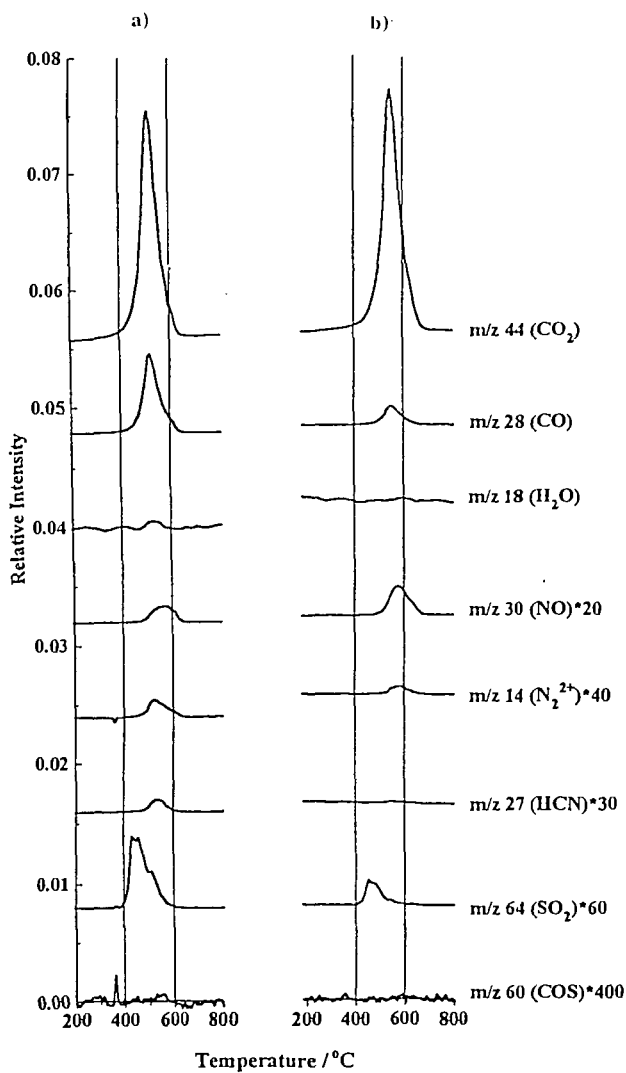


Figure 2 Temperature programmed combustion evolved gas profiles for Illinois No6 (Argonne) EFR char (HTT 1273 K) in 20 % oxygen/ helium with gas sampling a) directly above the sample and b) at the exit of the thermogravimetric analyser.

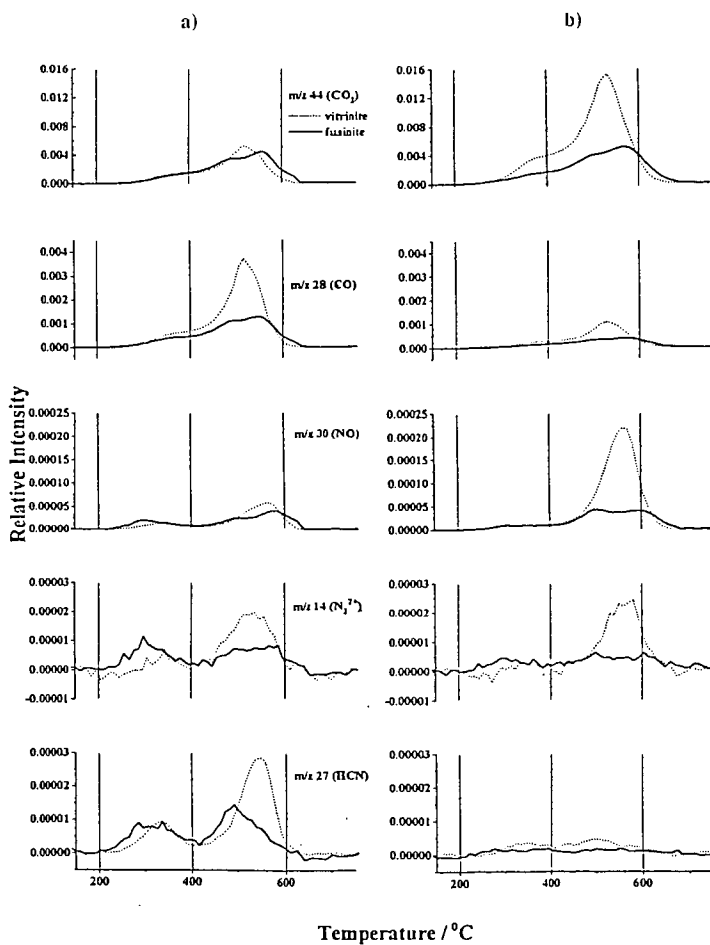


Figure 3 Temperature programmed combustion evolved gas profiles for maceral concentrates derived from coal A in 20 % oxygen/ helium with gas sampling a) directly above the sample and b) at the exit of the thermogravimetric analyser.